Supporting Information for

Spectral studies of a Cr(PNP)-MAO system for selective ethylene trimerization catalysis: searching for the active species

Loi H. Do, Jay A. Labinger, John E. Bercaw**

Arnold and Mabel Beckman Laboratories of Chemical Synthesis, California Institute of Technology, Pasadena, California 91125.

Corresponding Authors: jal@caltech.edu (J.A.L.), bercaw@caltech.edu (J.E.B.)

Table of Contents **Page(s)**

Experimental S2-S6
Materials and General Methods S2
Physical Methods S2
Synthesis and Characterization S2-S4
Spectroscopic Studies of MAO Activation S4-S5
Ethylene Trimerization Trials S5-S6
Scheme S1. Synthesis of **PN^{C18}P** and compound **2** S7
Figure S1. Variable temperature ^{2}H NMR spectra of **2** S8
Figure S2. Kinetic analysis of **2**/MAO at –40°C S9
Figure S3. Single wavelength plot of **2**/MAO at 25°C S10
Figure S4. ^{2}H NMR spectra of **2**/MAO in chlorobenzene S11
Figure S5. EPR spectra of **2**/MAO at –40°C S12
Figure S6. EPR spectra of **2**/MAO at 25°C S13
Figure S7. EPR spectra of **2**/MAO in the presence and absence of ethylene S14
Table S1. Ethylene trimerization trials for **2**/MAO in different solvents S15
Table S2. Summary of UV-vis and EPR spectroscopic data S16
References S17

EXPERIMENTAL

Materials and General Methods

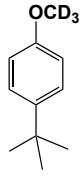
Commercial reagents were used as received without further purification. All air-sensitive manipulations were performed using standard Schlenk techniques or under a nitrogen atmosphere inside a Vac Atmosphere glovebox. Solvents were saturated with argon and either purified by passage through two columns of activated alumina or dried over CaH_2 followed by vacuum distillation. The chromium compound $CrCl_3(PN^{Me}P)$ (**1**) was prepared according to literature procedure.[1,2] The PNP ligands have methoxy-d_3 groups as ^2H NMR spectroscopic handles. The modified methylaluminoxane activator (MMAO-C4 solution in isohexanes, 7 wt % of Al, referred to as MAO in this paper) was obtained from Albemarle; it is a homogeneous solution that could be conveniently transferred quantitatively, unlike unmodified MAO, which is a heterogeneous slurry in solution. High-purity polymer grade ethylene was obtained from Air Liquide and purified by passage through a Matheson TriGas oxygen/moisture purifying column. Ethylene trimerization reactions were carried out using a Büchi miniclave high-pressure reactor equipped with a 300 mL glass vessel.

Physical Methods

NMR spectra were recorded on either a 300 or 500 MHz Varian Mercury spectrometer. Chemical shifts for $^1H/^{13}C$ NMR spectra were referenced to residual solvent peaks. ^{31}P NMR spectra were referenced externally to neat phosphoric acid (δ = 0.00 ppm) and ^2H NMR spectra were referenced externally to neat chloroform-d_3 (δ = 7.27 ppm) or internally to PhCl (δ = 7.00 ppm). Electrospray ionization (ESI) mass spectra were obtained using an Agilent Technologies 1100 Series MSD Trap via direct injection. UV-visible (UV-vis) absorption spectra were acquired on a Cary 50 spectrophotometer. Low temperature UV-vis spectroscopic studies were performed using a Unisoku cryostat to control the sample cell temperature and kinetic data were acquired using the Cary Scanning Kinetics program. X-band electron paramagnetic resonance (EPR) spectra were recorded on a Bruker 113 EMX spectrometer at –196°C in liquid nitrogen using a quartz finger dewar at 9.3 GHz (modulation frequency = 100 kHz, modulation amplitude = 2 G) in perpendicular mode. EPR signals were quantified by double integration and referenced to **2** and (2,2,6,6-Tetramethylpiperidin-1-yl)oxyl (TEMPO) for S = 3/2 and S = 1/2 species, respectively. Gas chromatography (GC) was performed using an Agilent 6890N instrument equipped with a flame ionization detector (FID). Analysis of ethylene trimerization reaction products was performed using a DB-1 capillary column (10 m length, 0.10 mm diameter, 0.40 μm film) with the following heating method: hold at 40°C for 3 min, ramp temperature at 50°C/min to 290°C and then hold for 3 min (total run time = 13 min). Biphenyl was used as an internal GC standard.

Synthesis and Characterization

4-*Tert*-butylanisole-d_3 (8). Potassium hydride (9.60 g, 0.240 mol) was suspended in 400 mL of dry tetrahydrofuran in a Schlenk flask and then was cooled to 0°C. Solid 4-*tert*-butylphenol (30.0 g, 0.200 mol) was added slowly portionwise. After stirring for ~1 h, the reaction mixture was treated with methyl iodide-d_3 (30.5 g, 0.210 mol). A reflux condenser was attached to the Schlenk flask and the reaction mixture was stirred at 65°C for ~15 h. The reaction was quenched by addition of a small amount of water and then



evaporated to dryness. About 400 mL of dichloromethane was added and then the mixture was washed with water (3 x 200 mL). The organic phase was separated, dried over $MgSO_4$, filtered, and evaporated to a colorless oil (30.13 g, 90%). ^{1}H NMR ($CDCl_3$, 500 MHz): δ 1.45 (s, 9H), 6.98 (d, J_{HH} =10 Hz, 2H), 7.44 (d, J_{HH}=10 Hz, 2H) ppm. ^{2}H NMR ($CDCl_3$, 77 MHz): δ 3.88 ppm. ^{13}C NMR ($CDCl_3$, 125 MHz): δ 31.78, 34.24, 54.48, 113.55, 126.40, 143.41, 157.57 ppm. GC-MS = 167.1 $[M]^+$ (Calcd = 167.1 $[M]^+$).

2-Bromo-4-*tert*-butylanisole-d_3 (**9**). 4-*Tert*-butylanisole-d_3 (**8**) (30.13 g, 0.180 mol) was dissolved in 300 mL of dichloromethane in a 500 mL round bottom flask and cooled to 0°C. A 50 mL dichloromethane solution containing bromine (9.51 mL, 0.186 mol) was added dropwise using an addition funnel over the course of ~1 h. The reaction mixture was stirred at room temperature for ~15 h and then washed with saturated aqueous sodium thiosulfate (3 x 100 mL). The organic layer was separated, dried over $MgSO_4$, filtered, and evaporated to a light yellow oil. The crude material was purified by silica gel column chromatography (80% hexane/20% CH_2Cl_2) to afford a colorless oil (40.0 g, 90%). ^{1}H NMR ($CDCl_3$, 500 MHz): δ 1.34 (s, 9H), 6.86 (d, J_{HH} = 10 Hz, 1H), 7.31 (d, J_{HH} = 10 Hz, 1H), 7.61 (d, 1H) ppm. ^{2}H NMR ($CDCl_3$, 77 MHz): δ 3.85 ppm. ^{13}C NMR ($CDCl_3$, 125 MHz): δ 31.55, 34.20, 55.45, 111.35, 111.65, 125.26, 130.48, 144.99, 153.67 ppm. GC-MS = 245.1.1 $[M]^+$ (Calcd = 245.0 $[M]^+$).

Bis(2-methoxy-d_3-4-*tert*-butylphenyl)(diisopropylamido)phosphine (**10**). Solid 2-bromo-4-tert-butylanisole-d_3 (**9**) (6.30 g, 25.6 mmol) was dissolved in 250 mL of dry tetrahydrofuran in a 500 mL Schlenk flask under an Argon atmosphere. The flask was cooled to -78°C using an acetone/dry ice bath and the reaction mixture was treated with *n*-butyllithium (1.6 M, 16 mL, 25.6 mmol) via slow syringe addition. After 1 h, a 10 mL solution of dichloro(diisopropylamido)phosphine (2.59 g, 12.8 mmol) in tetrahydrofuran was cannula transferred into the reaction flask and the resulting mixture was stirred for ~1 h at room temperature. The reaction mixture was evaporated to a yellow oil and the crude material was purified by alumina column chromatography, eluting with a solvent gradient of 100% hexane to 80% hexane/20% dicholoromethane. The final product was isolated as a colorless oil that solidified into a white solid upon standing at room temperature (2.50 g, 42%). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 1.12 (d, J_{HH} = 6 Hz, 12H), 1.22 (s, 18H), 3.34 (m, 2H), 6.69 (m, 2H), 7.26 (m, 4H) ppm. ^{2}H NMR ($CDCl_3$, 77 MHz): δ 3.63 ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ 23.82, 31.55, 34.25, 47.42, 54.87, 108.6, 125.48, 127.70 (d, J_{CP} = 12 Hz), 130.05, 142.44, 158.31 (d J_{CP} = 12 Hz) ppm. ^{31}P NMR ($CDCl_3$, 121 MHz): δ 18.25 ppm. ESI-MS(+) = 464.4 $[M+H]^+$ (Calcd = 464.5 $[M+H]^+$).

Bis(2-methoxy-d_3-4-*tert*-butylphenyl)chlorophosphine (**11**). Solid bis(2-methoxy-d_3-4-*tert*-butylphenyl)(diisopropylamido)phosphine (**10**) (3.59 g, 7.74 mmol) was dissolved in 300 mL of dry diethyl ether in a 500 mL Schlenk flask under an Argon atmosphere. Upon slow addition of a solution of hydrogen chloride (2.0 M in diethyl ether, 8.1 mL, 16.2 mmol), instantaneous formation of a white precipitate was observed. After stirring at room temperature for 1h, the colorless solution was cannula filtered into a fresh Schlenk flask and then evaporated under vacuum to give a white solid (2.20 g, 71%). The solid was isolated and stored

inside the glovebox. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 1.21 (s, 18H), 6.79 (m, 2H), 7.38 (m, 4H) ppm. ^{2}H NMR ($CDCl_3$, 77 MHz): δ 3.71 ppm. ^{13}C NMR ($CDCl_3$, 125 MHz): δ 30.78, 31.31, 55.02, 110.09, 125.11 (d, J_{CP} = 22 Hz), 128.49, 129.45, 143.32, 158.86 (d, J_{CP} = 12 Hz) ppm. ^{31}P NMR ($CDCl_3$, 121 MHz): δ 72.94 ppm.

Bis(bis(2-methoxy-*d*$_3$-4-*tert*-butylphenyl)phosphino)octadecylamine ($PNC^{18}P$). Octadecylamine (0.352 g, 1.31 mmol) and triethylamine (1.32 g, 13.1 mmol) were dissolved in 4.0 mL of dry chloroform in a thick-walled glass reaction tube. Solid bis(2-methoxy-*d*$_3$-4-*tert*-butylphenyl)chlorophosphine (**11**) (1.07 g, 2.68 mmol) was added and the tube was sealed with a Teflon screwcap. The reaction mixture was then stirred at 90°C for ~20 h. The reaction was quenched by the addition of 10 mL of water and the organic product was extracted into dichloromethane (3 x 20 mL). The organic layer was separated, dried over $MgSO_4$, filtered, and then evaporated to a yellow oil. The crude material was purified by alumina column chromatography, eluting with a solvent gradient of 10% dichloromethane/90% hexane to 50% dichloromethane/50% hexane. The final product was isolated as an air-stable colorless oil (0.377 g, 29%). ^{1}H NMR ($CDCl_3$, 500 MHz): δ 0.90-1.12 (m, 71H), 3.25 (m, 2H), 6.70 (m, 4H), 7.22-7.28 (m, 8H) ppm. ^{2}H NMR ($CDCl_3$, 77 MHz): δ 3.43 ppm. ^{13}C NMR ($CDCl_3$, 125 MHz): δ 14.43, 23.00, 27.56, 29.68-30.01, 31.68, 32.23, 34.30, 55.71, 109.97, 126.44, 128.14, 131.37, 142.56, 159.10 ppm. ^{31}P NMR ($CDCl_3$, 121 MHz): δ 41.03 ppm. ESI-MS(+) = 994.6 $[M+H]^+$ (Calcd = 994.8 $[M+H]^+$).

$CrCl_3(PN^{C18}P)$ (2). Inside the glovebox, the $PN^{C18}P$ ligand (830 mg, 835 μmol) and $CrCl_3(THF)_3$ (313 mg, 835 μmol) were dissolved in 4 mL of dry dichloromethane and stirred at room temperature for 20 h. The dark blue solution was evaporated to dryness, giving a blue solid (900 mg, 95%). UV-vis (CH_2Cl_2): λ_{max} = 500 (312 $cm^{-1}M^{-1}$), 660 (591 $cm^{-1}M^{-1}$) nm. ^{2}H NMR (PhCl, 77 MHz, RT): δ 4.31, 7.80 (b) ppm. Anal. Calcd. for $CrC_{62}H_{85}D_{12}Cl_3NO_4P_2$: C, 64.60; H, 9.53; N, 1.22; Found: C, 62.78/62.59; H, 8.56/8.65; N, 1.14/1.15. *Similar elemental analysis results were obtained after multiple independent measurements after drying under high vacuum. It is conceivable that the complex forms a solvate with dichloromethane. No obvious impurities were detected from measurements by various spectroscopic methods.*

Spectroscopic Studies of MAO Activation

UV-vis absorption spectroscopy: A 4.0 mL aliquot of **2** (473 or 946 μM) in chlorobenzene was added to a quartz cuvette containing a micro stir bar and sealed with a rubber septum. The cuvette was placed inside a temperature-controlled sample holder and set to the desired temperature with moderate stirring. The scanning kinetics program was started and ~100 mg of the MAO solution was injected using a gas-tight syringe. Each dataset was recorded over the course of several hours. The kinetic data were fit using the program Kaleidagraph.

EPR spectroscopy (without ethylene): To prepare **2**, 50 μL of chlorobenzene and 150 μL solution of 6.67 mM **2** were added to an EPR tube, giving an effective concentration of 5.0 mM in Cr,

and sealed with a rubber septum. To prepare samples of the intermediates, 50 μL of MAO (diluted in a chlorobenzene:MAO mixture with a ratio of 2:1) was added to an EPR tube and sealed with a rubber septum. To keep the EPR tube temperature sufficiently low during mixing, about 3/4 of the tube was immersed in liquid nitrogen using a dewar. A 150 μL solution of 6.67 mM **2** was then injected, causing the blue solution to freeze inside the top portion of the EPR tube. The tube was then removed from the liquid nitrogen bath and allowed to thaw while oriented horizontally so that the MAO reagent and **2** do not mix. Once both solutions were free flowing, the tube was turned upright and gently agitated to mix and then immediately placed in a –40°C cooling bath. Upon reaction of **2** with MAO at –40°C, the solution color instantaneously changed from blue to red and then gradually an olive green. The sample was frozen in liquid nitrogen at the appropriate time point to trap the various colored-intermediates for EPR measurements. All samples were recorded at –196°C.

EPR spectroscopy (with ethylene): NMR tubes with septum screwcaps were used in place of standard EPR tubes because of their wider tube diameter and ability to provide a better seal. Although the NMR tubes display a paramagnetic impurity centered at approx. $g = 4.0$, it did not obscure the region of interest at $g = 2.0$. A similar procedure was used to prepare the samples for EPR measurements as described above with a few modifications: 1) **2** was first saturated with ethylene by bubbling the chlorobenzene stock solution with high-purity ethylene gas for 5 min; 2) the NMR tubes were pre-saturated with ethylene by inserting a long needle through the septum into the bottom of the tube with a steady stream of ethylene gas, 3) a constant pressure of ethylene (~1 atm) was maintained inside the NMR tubes after mixing **2** with MAO.

^{2}H NMR spectroscopy: To prepare **4/5**, about 27 mg of **2** was dissolved in 500 μL of chlorobenzene in an NMR tube and sealed with a septum screwcap. The NMR tube was cooled to -40°C inside the NMR spectrometer. The tube was ejected and then 150 mg of MAO was added to **2** using a gas-tight syringe while the solution was still cold. The tube was immediately placed back into the spectrometer and the temperature was continued to be maintained at –40°C. The reaction progress was followed over the course of several hours by recording sets of 256 scans until no changes were observed. The red species **3** was too short-lived on the NMR acquisition timescale to be measured. To prepare **6/7**, the **2**/MAO sample was warmed to room temperature for 1 h and then cooled to -40°C to be recorded.

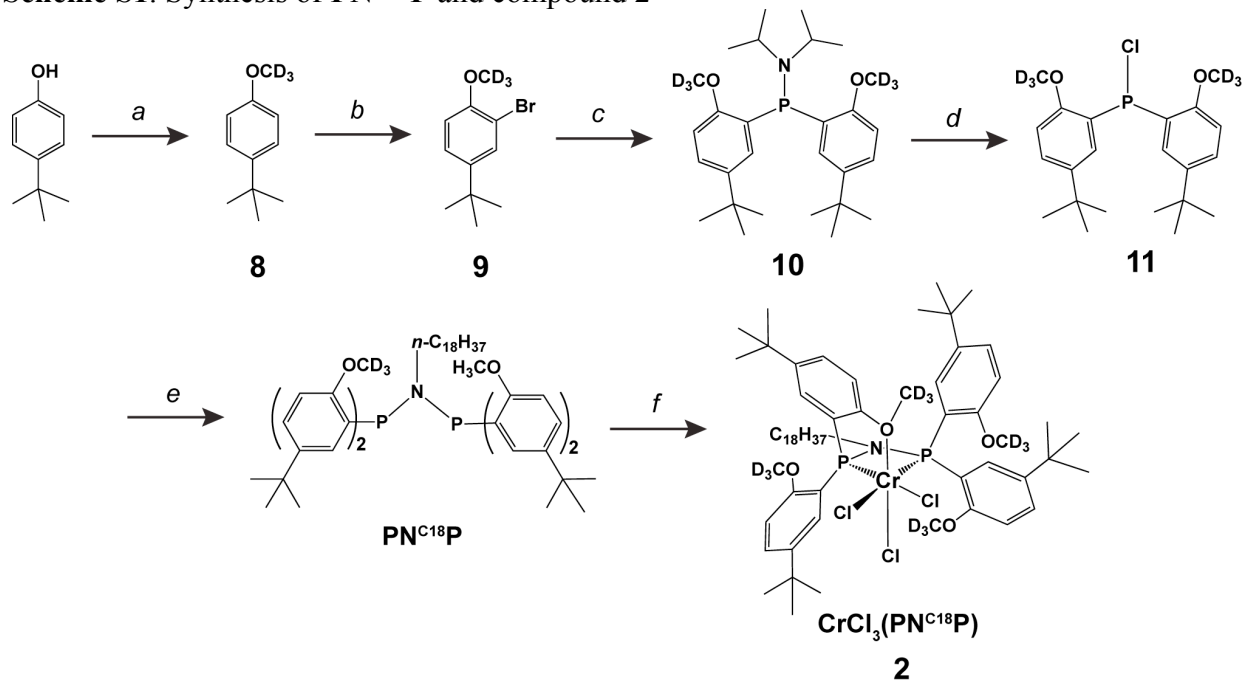
Ethylene Trimerization Trials

Method I: Inside the glovebox, the chromium pre-catalyst (11.8 μmol) was dissolved in 25 mL of dry chlorobenzene and then the mixture was transferred to a Büchi miniclave reactor. The reactor was sealed, attached to a high-pressure gas manifold, and then placed in a temperature control bath (water bath for 25°C or acetonitrile/dry ice bath for –40°C). The vessel was then pressurized with 50 psi of ethylene. A gas-tight syringe was used to add 250 mg of MAO through a side-arm equipped with a septum screwcap. The reaction was allowed to proceed for 1 h and then quenched by the addition of aqueous HCl. Solid biphenyl was added (50 mg) and a 1.0 mL aliquot of the organic layer was filtered through a silica gel pipette plug and then analyzed by GC.

Method II: Inside the glovebox, the chromium pre-catalyst (11.8 μmol) was dissolved in 25 mL of dry chlorobenzene and then the mixture was transferred to a Büchi miniclave reactor. The reactor was sealed and then placed in a room temperature water bath. A gas-tight syringe was used to add 250 mg of MAO through a side-arm equipped with a septum screwcap. After a 15 s activation period, in which the solution appeared green, the vessel was then pressurized with 50 psi of ethylene. The reaction was allowed to proceed for 1 h and then quenched by the addition of aqueous HCl. Solid biphenyl was added (50 mg) and a 1.0 mL aliquot of the organic layer was filtered through a silica gel pipette plug and then analyzed by GC.

Method III: Inside the glovebox, the chromium pre-catalyst (11.8 μmol) and MAO (250 mg) were dissolved in 25 mL of dry chlorobenzene and stirred for ~15 h, giving a light blue-green colored solution. The mixture was then transferred to a Büchi miniclave reactor. The reactor was sealed, attached to a high-pressure gas manifold, and then pressurized with 50 psi of ethylene. The reaction was allowed to proceed for 1 h and then quenched by the addition of aqueous HCl. Solid biphenyl was added (50 mg) and a 1.0 mL aliquot of the organic layer was filtered through a silica gel pipette plug and then analyzed by GC.

Scheme S1. Synthesis of **PN^{C18}P** and compound **2**



a) *i.* NaH, THF, *ii.* CD_3I; *b*) Br_2, CH_2Cl_2; c) *i.* nBuLi, THF, *ii.* dichloro(diisopropylamido)-phosphine; *d*) HCl, Et_2O; *e*) octadecylamine, triethylamine, $CHCl_3$; *f*) $CrCl_3(THF)_3$, CH_2Cl_2.

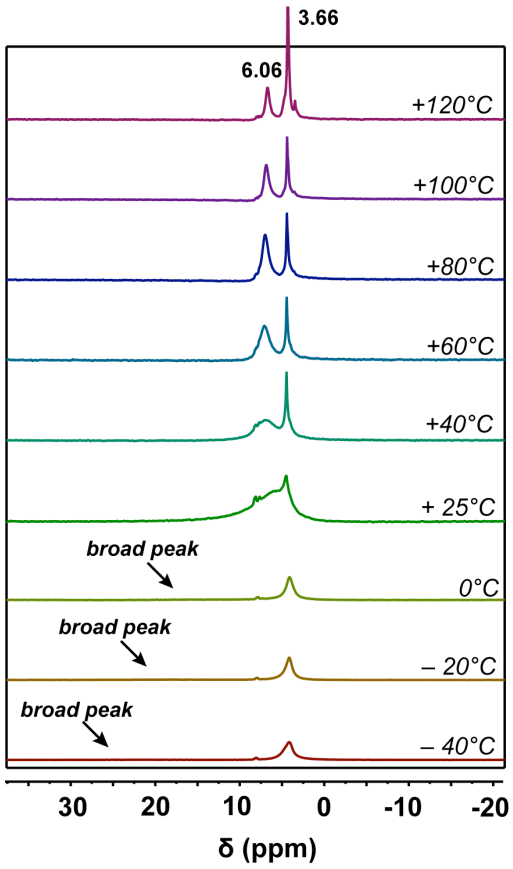


Figure S1. Variable temperature ^{2}H NMR spectra of **2** (~4 mM) in chlorobenzene.

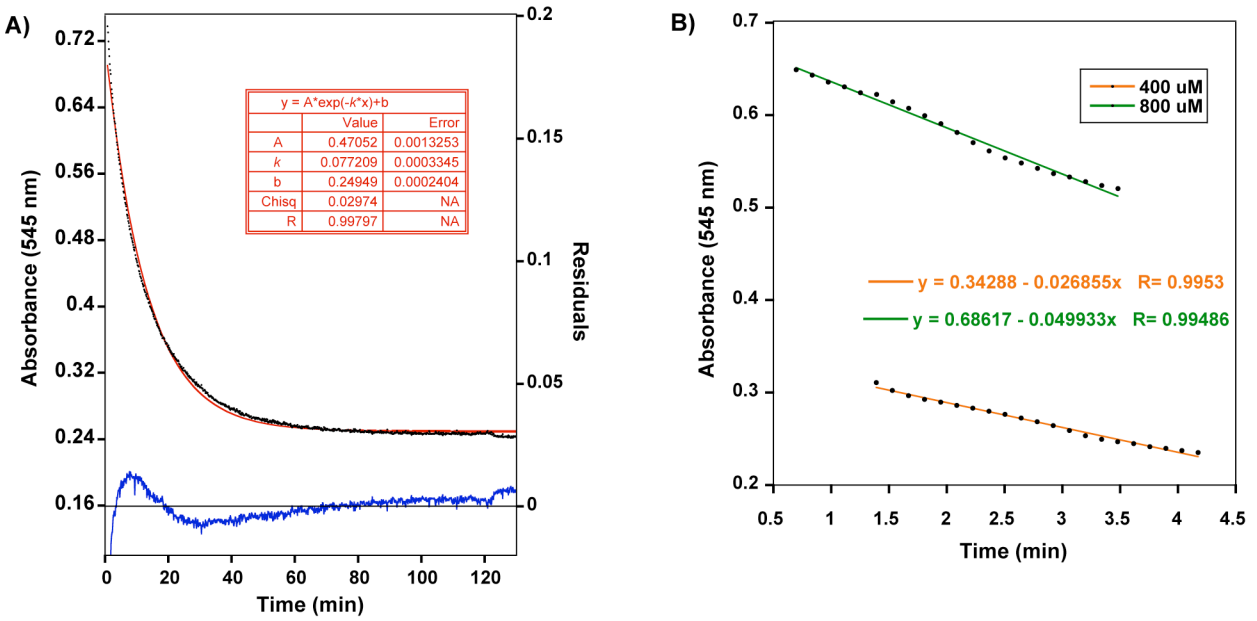


Figure S2. A) Single wavelength plot (545 nm) showing the absorbance change from reaction of **2**/MAO at –40°C (black dots). See Figure 1B for the full spectra. The data were fit satisfactorily to a single-exponential decay function (red trace), with a k_{obs} = ~0.08 min^{-1}. The fit residual is shown in blue. B) The absorbance changes at 545 nm for two different concentrations of **2** (400 µM and 800 µM)/MAO, at early time points, were fit to linear functions. The rates were calculated to be 0.03 M/min (orange line) and 0.05 M/min (green line) for the 400 µM and 800 µM solution of **2**, respectively, suggesting that the conversion of **3** to **4** is approximately first-order in the chromium complex.

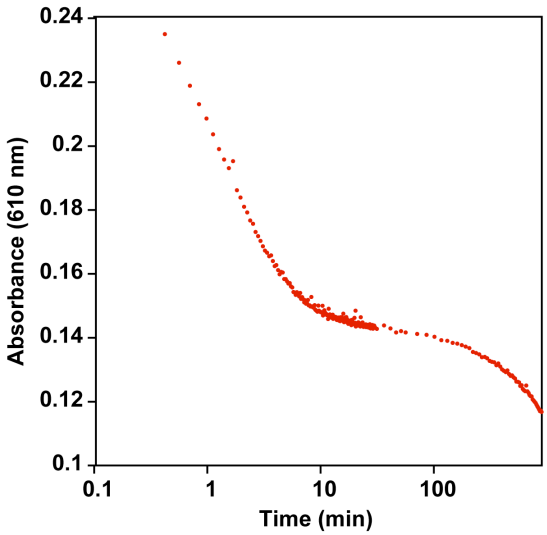


Figure S3. Single wavelength plot (610 nm) showing the absorbance change from reaction of **2**/MAO at 25°C (red dots). See Figure 1C for the full spectra. The data could not be fit to simple kinetic functions. The abscissa is displayed on a log scale.

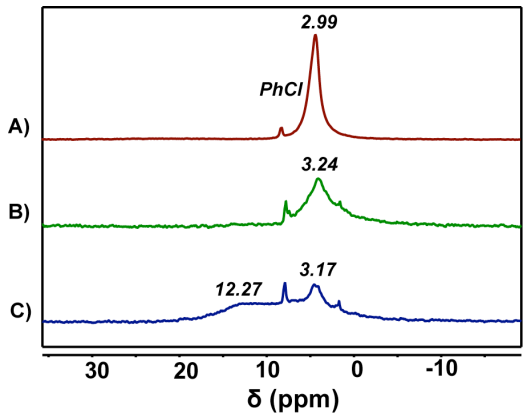


Figure S4. ^{2}H NMR spectra of: A) 5 mM **2** in chlorobenzene , B) after addition of MAO to **2** at –40°C, and C) after further warming to room temperature. All spectra were recorded at –40°C and referenced internally to residual chlorobenzene at ~7.00 ppm.

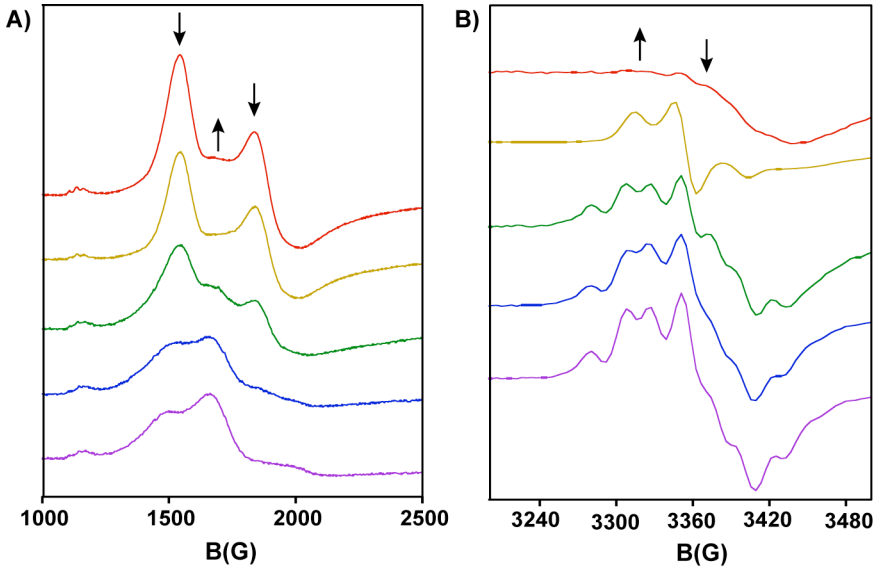


Figure S5. X-band EPR spectra obtained after mixing **2** with MAO at –40°C in chlorobenzene and then frozen at various time points. Part A shows the region from 1000-2500 G and part B shows 3200-3500 G. The spectra shown correspond to mixing after 0 s (red), 30 s (yellow), 30 min (green), 1 h (blue), and 2 h (purple). The spectral changes are indicated by arrows. All spectra were recorded at –196°C.

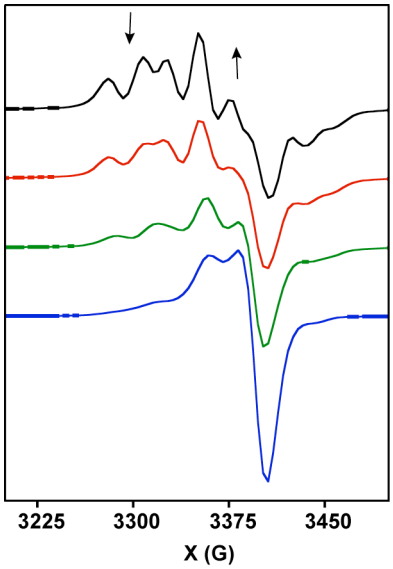


Figure S6. X-band EPR spectra obtained after mixing **2** with MAO at 25°C in chlorobenzene and then frozen at various time points. The spectra correspond to mixing after 10 s (black), 5 min (red), 20 min (green), and 15 h (blue). The spectral changes are indicated by arrows. All spectra were recorded at –196°C.

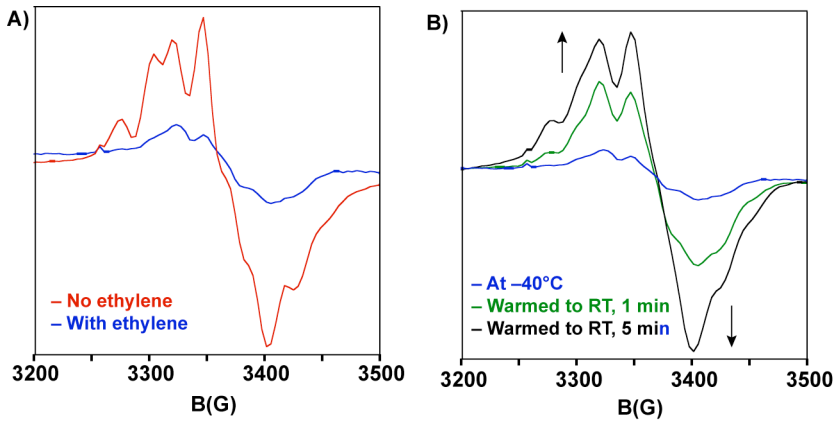


Figure S7. X-band EPR spectra of A) the reaction product of **2**/MAO in the presence (blue trace) and absence (red trace) of ethylene at –40°C; B) the reaction product of **2**/MAO in the presence of ethylene warmed to RT. The spectral changes are indicated by arrows. All spectra were recorded at –196°C.

Table S1. Ethylene trimerization trials for **2**/MAO in various solvents

Entry[a]	**Solvent**	**Activity** (g trimers/g Cr/h)	**1-Hexene** (wt %)	**Higher trimers** (wt %)	**Polymer** (g)
1	CH_2Cl_2	0	0	0	0
2	Et_2O	0	0	0	0
3	*o*-PhF_2	3260	80	20	0.20 g
4	PhCl	1446	90	10	0.82 g
5	Toluene	487	96	4	0.65 g

[a]Reaction condition: dissolve complex **2** (11.8 μmol) in 25 mL of solvent, pressurize reactor with 50 psi of ethylene and then add MAO (250 mg, ~500 equiv).

Table S2. Summary of EPR and UV-vis spectroscopic data

	EPR[a]			UV-vis[d]
Species	**S**	***g* values[b]**	**% Cr_{Total}[c]**	**λ_{max} (nm)**
2	3/2	1.99, 3.02, 4.57, (5.86)	100	500, 660
3	3/2	1.98, 3.50, 4.34, (5.90)	100	540
4	3/2	3.85, 4.17, 4.50, (5.80)	98	448, 630
5	1/2	1.98, 2.00, 2.03	< 2	*N/A*
6	1/2	1.98, 2.00	6	*N/A*
7		*EPR silent*	*94*	*N/A*

[a]Recorded as a frozen PhCl solution at -196°C. [b]*g*-values in parentheses are due to spin-forbidden transitions. [c]Integration determined from either **2** (for S=3/2 signals) or TEMPO (for S=1/2 signals). [d]Recorded in chlorobenzene at –40°C.

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